



(11) EP 1 027 930 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:
16.08.2000 Bulletin 2000/33

(21) Application number: 98941804.1

(22) Date of filing: 09.09.1998

(51) Int. Cl.⁷: B01J 29/064, B01J 29/10,
B01J 29/20, B01J 29/42,
B01J 29/66, B01D 53/94,
F01N 3/08

(86) International application number:
PCT/JP98/04072

(87) International publication number:
WO 99/13981 (25.03.1999 Gazette 1999/12)

(84) Designated Contracting States:
DE FR GB

(30) Priority: 12.09.1997 JP 24871297
12.09.1997 JP 24870597
07.10.1997 JP 27429997

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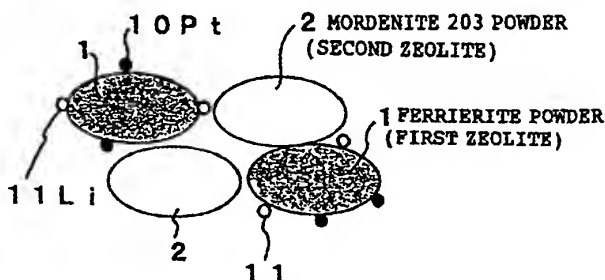
(54) EXHAUST EMISSION CONTROL CATALYST

(57) It is arranged such that a first zeolite loaded with a catalyst metal and a second zeolite unloaded with a catalyst metal are mixed.

By actively adsorbing HC onto the second zeolite, it is possible to inhibit the catalyst metal loaded on the first zeolite from being poisoned by HC, and to sufficiently

adsorb HC. Accordingly, since the HC adsorbing capability is improved, and since the HC poisoning of the catalyst metal is suppressed, the NO_x purifying capability is enhanced and the durability is also upgraded.

FIG. 2



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Description

Technical Field

5 [0001] The present invention relates to a catalyst for purifying an exhaust gas, catalyst which is used in an exhaust system of an automobile to purify harmful components in the exhaust gas, more particularly to an HC-adsorption type NO_x-selective-reduction type catalyst that can selectively reduce and remove NO_x in an oxygen-rich exhaust gas, which is emitted from a diesel engine, or the like, by HC adsorbed on a zeolite support.

10 Background Art

[0002] As an NO_x-selective-reduction type catalyst that selectively reduces NO_x and purifies them, a catalyst for purifying a diesel exhaust gas has been known which is made by loading a catalyst metal on a zeolite. Since the zeolite has many acidic sites so that it is acidic, it is good in terms of the HC adsorbing capability and adsorbs HC in the exhaust gas. Therefore, even in an oxygen-rich exhaust gas, such as the diesel exhaust gas, the atmosphere becomes a stoichiometric or a rich atmosphere, in which HC are abundant, adjacent to the catalyst, and NO_x react with the adsorbed HC and are thereby reduced and purified by the catalytic action of the loaded catalyst metal.

15 [0003] Further, the zeolite exhibits a cracking action, and zeolites, such as mordenite, ZSM-5, an ultra-stable and type "Y" zeolite (US-Y), exhibit an especially high cracking action. Therefore, by using these zeolites as a catalyst support, the SOF (Soluble Organic Fraction) in the diesel exhaust gas are subjected to cracking, and become low-molecular HC, which are more likely to react, and thus the NO_x can be reduced and purified more efficiently.

20 [0004] Furthermore, by injecting HC, such as a light oil and propane, into the diesel exhaust gas, the exhaust gas atmosphere is turned into a stoichiometric or a rich atmosphere, and thereby the NO_x purifying capability is enhanced. In this case as well, by using a zeolite support, the atmosphere adjacent to the catalyst becomes a rich atmosphere in which HC are more abundant, and accordingly the NO_x purifying capability is further improved.

25 [0005] In HC-adsorption type catalysts in which a zeolite is used as a support, improving the HC adsorbing capability would result in improving the NO_x purifying capability. However, according to recent studies, it has been revealed that upgrading the HC adsorption capability does not necessarily result in improving the NO_x purifying capability.

30 [0006] One of the causes for this is that the so-called HC poisoning of the catalyst metal occurs when the adsorbed HC are desorbed to adsorb onto the catalyst metal, such as Pt, or the like, and the activity of the catalyst metal decreases.

[0007] Further, the zeolite is a tectaluminosilicate chemically, and zeolites having a variety of Si/Al ratios have been known. And it has been understood that the characteristics of zeolites depend greatly on the values of this Si/Al ratio.

35 [0008] Since a zeolite having a small Si/Al ratio has many acidic sites and exhibits a high cracking capability and a high HC adsorption capability, a catalyst made by loading a catalyst metal on this is good in terms of the NO_x purifying capability. However, in the zeolite having many acidic sites, the HC adsorbed in the pores are carbonized to cause the caulking easily, and they close the insides of the pores, and as a result, there is a drawback in that the HC adsorbing capability decreases chronologically.

40 [0009] Further, a zeolite having many acidic sites loses the acidic sites easily by de-Al (The 4-coordination is turned into the 6-coordination in the zeolite structure.) when it is subjected to a hydrothermal durability test, there arises a drawback in that the cracking capability decreases. Furthermore, in the catalyst in which a catalyst metal is loaded on such a zeolite, by the de-Al resulting from the hydrothermal durability test, the catalyst metal grows granularly so that the activity decreases considerably and there arises a drawback in that the durability is low.

45 [0010] Whilst, a zeolite having a large Si/Al ratio has advantages in that, since it is less likely to be subjected to the de-Al and since the granular growth of the catalyst metal resulting from the de-Al is suppressed, it is good in terms of the durability. However, in the zeolite having a large Si/Al ratio, since the acidic sites exist less, the adsorbing capability and the cracking capability are low so that there is a problem in that the NO_x purifying capability is low initially.

50 [0011] By the way, sulfur oxides (SO_x), which result from the combustion of the sulfur components in the fuel, are contained in the exhaust gas, and there arises a drawback in that the catalytic activity of the catalyst metal decreases when these SO_x components adsorb onto the catalyst metal (especially, Pt). This is referred to as the SO_x poisoning.

[0012] As a method for inhibiting the SO_x poisoning, it is possible to think of a method in which an alkaline component, such as an alkali metal and an alkaline-earth metal, is loaded together with the catalyst metal. Namely, since SO_x is more likely to adsorb onto the alkaline component than onto the catalyst metal, such as Pt, the SO_x poisoning of the catalyst metal is suppressed, and the high catalytic activity is maintained.

55 [0013] However, when the alkaline component is loaded, the SO_x poisoning of the catalyst metal is suppressed, but the alkaline component is loaded onto the acidic sites of a zeolite preferentially. Therefore, the neutralization results in the disappearance of the acidic sites, and there arises a drawback in that the major characteristics of a zeolite, i.e., the HC adsorbing capability and the cracking capability, decrease.

[0014] The present invention has been developed in view of these situations, and it is a major object of the present invention to make an HC-adsorption type exhaust-gas-purifying catalyst which exhibits a high NO_x purifying capability initially and which can maintain the high conversion after a durability test.

5 [0015] Further, it is a secondary object of the present invention to further improve the NO_x purifying capability by suppressing the HC poisoning of the catalyst metal while improving the HC adsorbing capability.

[0016] Furthermore, it is a further object of the present invention to suppress the SO_x poisoning of the catalyst metal, and also to suppress the decrement of the high HC adsorbing capability and the high cracking capability of a zeolite.

10 Disclosure of Invention

[0017] It is a characteristic of an exhaust-gas-purifying catalyst solving the aforementioned assignments and set forth in Claim 1 that it is a catalyst reducing and purifying nitrogen oxides in an oxygen rich atmosphere which contains oxygen more than necessary for oxidizing components to be oxidized in the exhaust gas by hydrocarbon (HC) adsorbed on a zeolite support, wherein:

the zeolite support comprises a first zeolite loaded with a catalyst metal and a second zeolite free from loading a catalyst metal.

20 [0018] It is a characteristic of an exhaust-gas-purifying catalyst set forth in Claim 2 that, in the exhaust-gas-purifying catalyst set forth in Claim 1, the first zeolite has pores whose diameters are a predetermined value or less and the second zeolite has pores whose diameters exceed the predetermined value.

[0019] It is a characteristic of an exhaust-gas-purifying catalyst set forth in Claim 3 that, in the exhaust-gas-purifying catalyst set forth in Claim 2, the predetermined value is 5.5 Å.

25 [0020] It is a characteristic of an exhaust-gas-purifying catalyst set forth in Claim 4 that, in the exhaust-gas-purifying catalyst set forth in Claim 1, the first zeolite is 1/4-1/2 by weight ratio in all zeolites.

[0021] It is a characteristic of an exhaust-gas-purifying catalyst set forth in Claim 5 that, in the exhaust-gas-purifying catalyst set forth in claim 1, an alkaline component selected from the group consisting of alkali metals and alkaline-earth metals is further loaded on the first zeolite.

30 [0022] It is a characteristic of an exhaust-gas-purifying catalyst set forth in Claim 6 that, in the exhaust-gas-purifying catalyst set forth in Claim 1, a molar ratio of silicon with respect to aluminum (Si/Al) is larger in the first zeolite than in the second zeolite.

[0023] It is a characteristic of an exhaust-gas-purifying catalyst set forth in Claim 7 that, in the exhaust-gas-purifying catalyst set forth in Claim 6, a difference between the molar ratio (Si/Al) of the first zeolite and the molar ratio (Si/Al) of the zeolite is 200 or more.

35 [0024] It is a characteristic of an exhaust-gas-purifying catalyst set forth in Claim 8 that, in the exhaust-gas-purifying catalyst set forth in Claim 6, the first zeolite is 2/3-1/2 by weight ratio in all zeolites.

[0025] And, it is a characteristic of an exhaust-gas-purifying catalyst set forth in Claim 9 that, in the exhaust-gas-purifying catalyst set forth in Claim 6, the first zeolite employs mordenite exhibiting 200 or more, ZSM-5 exhibiting 1,000 or more, type "Y" zeolite exhibiting 400 or more, type "A" zeolite exhibiting 400 or more, ferrierite exhibiting 400 or more, or zeolite β exhibiting 200 or more by a molar ratio (Si/Al).

Brief Description of Drawings

45 [0026]

Fig. 1 is a graph for illustrating a load variation of a diesel engine which was used in evaluations on examples.

Fig. 2 is an explanatory diagram for schematically illustrating a structure of an exhaust-gas-purifying catalyst of an example according to the present invention.

50 Fig. 3 is a bar graph for illustrating maximum NO_x conversions which were exhibited by catalysts of examples and comparative examples initially and after a durability test.

Best Mode for Carrying Out the Invention

55 [0027] In the exhaust-gas-purifying catalyst set forth in Claim 1, the zeolite support is constituted by the first zeolite, on which the catalyst metal is loaded, and the second zeolite, which is free from the loading of the catalyst metal. On the first zeolite which is loaded with the catalyst metal, HC are oxidized by the catalyst metal, and adsorbed HC are considerably less. Therefore, in the exhaust-gas-purifying catalyst according to the present invention, HC in the exhaust

gas are mainly adsorbed onto the second zeolite.

[0028] On the other hand, on the first zeolite, NO is oxidized by the catalyst metal, and is turned into NO_x. There are released HC, which are adsorbed on the second zeolite, and accordingly the HC concentration adjacent to the first zeolite is heightened, NO_x are efficiently reduced and purified to N₂ by the reaction of NO_x and HC. Further, since the
5 SOF in the exhaust gas are cracked by the second zeolite to HC which have low molecular weights, and which are highly reactive, the aforementioned operations are effected further actively.

[0029] By these operations, the exhaust-gas-purifying catalyst set forth in Claim 1 exhibits high NO_x purifying performance.

[0030] As for the first zeolite and the second zeolite in the exhaust-gas-purifying catalyst set forth in Claim 1, it is
10 possible to use a natural or synthesized zeolite, such as mordenite, ZSM-5, type "Y" zeolite, type "A" zeolite, ferrierite, zeolite β. It is possible to use a single species which is selected from these, and it is also possible to mix and use a plurality of the species. Further, the materials of the first zeolite and the second zeolite can be different, and an identical zeolite can be used.

[0031] A ratio between the first zeolite and the second zeolite can preferably fall in the range of 1/4-1/2 by weight of
15 the first zeolite with respect to total zeolites. When the first zeolite is more than 1/2, there arises a drawback in that the HC adsorption capability cannot be secured sufficiently. Further, when the first zeolite is 1/4 or less with respect to the total zeolites, there arises a case where the dispersibility of the noble metal decreases.

[0032] As for the noble metal, it is possible to use a noble metal, such as platinum (Pt), rhodium (Rh), palladium (Pd), iridium (Ir) and silver (Ag). Further, depending on cases, it is possible to use a base metal, such as iron, cobalt
20 and nickel. It is possible to combinedly use the noble metal and the base metal.

[0033] A loading amount of the catalyst metal depends on the specific metals, however, for example, when it is platinum, it is possible to load on the first zeolite in an amount of 1-3 g with respect to 1 liter of a honeycomb catalyst support.

[0034] When producing the exhaust-gas-purifying catalyst according to the present invention, the first zeolite powder, which is loaded with a catalyst metal, and the second zeolite powder, which is free from the loading can be mixed
25 to make a mixture powder, and the mixture powder can be pelletized to make a pellet catalyst. Alternatively, this mixture powder can be coated on a honeycomb support substrate to make a honeycomb catalyst.

[0035] By the way, it has been revealed that the HC poisoning of the catalyst metal is likely to arise in higher HC species which have a relatively large number of carbon atoms. Accordingly, it is possible to suppress the HC poisoning
30 by inhibiting the higher HC species from contacting with the catalyst metal.

[0036] Whilst, by the studies of the present inventors, it has been found that there is a correlation between a pore diameter of a zeolite and the number of carbon atoms of HC (molecular weights) to be adsorbed in the pores. Namely, in pores of a small diameter, lower HC are mainly adsorbed which have small number of carbon atoms and which are less bulky molecularly, and in pores of a large diameter, higher HC are mainly adsorbed which have large number of
35 carbon atoms and which are more bulky molecularly.

[0037] Hence, according to the exhaust-gas-purifying catalyst set forth in Claim 2, in the exhaust-gas-purifying catalyst set forth in Claim 1, it is arranged so that the first zeolite has pores whose diameters are a predetermined value or less, and that the second zeolite has pores whose diameters exceed the predetermined value.

[0038] With this arrangement, since the higher HC, which have a large number of carbon atoms and which are bulky molecularly, are adsorbed mainly onto the second zeolite whose pore diameters exceed the predetermined value,
40 they contact with the catalyst metal with a lower probability, and the HC poisoning of the catalyst metal is suppressed.

[0039] Whilst, the lower HC, which have small number of carbon atoms and which are less bulky molecularly, are adsorbed mainly onto the first zeolite whose pore diameters are a predetermined value or less, react with NO_x by the catalytic action of the catalyst metal loaded therein, and reduce and purify the NO_x. Note that, since the lower HC,
45 which have small number of carbon atoms and which are less bulky molecularly, are highly active and are likely to be oxidized independently, they are not expected to react with NO_x when they are adsorbed away from the catalyst metal. However, in the catalyst set forth in Claim 2, since the catalyst metal is loaded on the first zeolite which has the pores of a predetermined value or less, the lower HC, which have small number of carbon atoms and which are less bulky molecularly, are adsorbed onto the first zeolite, and since the HC are in proximity to the catalyst metal sufficiently, the
50 adsorbed HC react with the NO_x by the catalytic action of the catalyst metal so that the NO_x are efficiently reduced and purified.

[0040] Further, the higher HC, which are adsorbed onto the second zeolite whose pore diameter exceeds the predetermined value, which have a large number of carbon atoms and which are bulky molecularly, are subjected to cracking by the zeolite, the number of carbon atoms decreases, and become less bulky molecularly. Accordingly, the HC
55 subjected to the cracking are easily desorbed from the pores of the second zeolite, are adsorbed onto the first zeolite, and react with the NO_x by the catalytic action of the catalyst metal so that the NO_x are reduced and purified.

[0041] As for the specific value of the aforementioned predetermined value, it is possible to employ it in a trial-and-error manner dependently on the types of the catalyst metal and the temperatures of the exhaust gas. However, as for

the HC species which cause the HC poisoning to the catalyst metal, HC having a side chain, aromatic cyclic HC, etc., are listed. The molecular diameters of these HC species exceed 5.5 Å mostly. Further, HC species, which do not cause the HC poisoning to the catalyst metal, are linear HC, such as propane, butane, etc., and the molecular diameters of these HC species 5 Å or less mostly. Hence, as set forth in Claim 3, it is preferred that, as for the first zeolite, a zeolite whose pore diameter is 5.5 Å or less is used, and that, as for the second zeolite, a zeolite whose pore diameter exceeds 5.5 Å is used.

[0042] For example, since the average pore diameter of ferrierite is 4.8 Å, the average pore diameter of ZSM-5 is 5.5 Å, the average pore diameter of mordenite is 7 Å, the average pore diameter of US-Y (type "Y") zeolite is 7.8 Å and the average pore diameter of zeolite β is 8.0 Å, it is preferred that, as for the first zeolite, ferrierite, ZSM-5, etc., are used, and that, as for the second zeolite, mordenite, US-Y, zeolite β, etc., are used.

[0043] A plurality of zeolites can be used for the first zeolite and/or the second zeolite. If such is the case, an average value of the pores of the plurality of zeolites can be taken as the pore diameter of the first zeolite and/or the second zeolite.

[0044] According to the exhaust-gas-purifying catalyst set forth in Claim 5, in the exhaust-gas-purifying catalyst set forth in Claim 1, an alkali component is further loaded on the first zeolite in addition to the catalyst metal. Hence, as described above, the SO_x poisoning of the catalyst is suppressed by the alkali component. However, since the alkali component is loaded onto the acidic sites of the first zeolite preferentially, the first zeolite itself is low in terms of the HC adsorbing capability and the cracking capability.

[0045] Accordingly, in the exhaust-gas-purifying catalyst set forth in Claim 5, the second zeolite is mixed with respect to the first zeolite loaded with the alkali component, and is used. Since no alkali component is loaded onto this second zeolite, a high HC adsorbing capability and a cracking capability are secured by the second zeolite. Namely, the SOF in an exhaust gas are cracked mainly by the second zeolite, and the generated HC and the HC in the exhaust gas are adsorbed mainly onto the second zeolite.

[0046] Whilst, the NO_x in the exhaust gas are further oxidized partly on the surface of the catalyst metal by oxygen existing in the exhaust gas, but are reduced and purified to N₂ on the surface of the catalyst metal by the HC released from the second zeolite.

[0047] And, since the SO_x poisoning of the catalyst metal is suppressed by the alkali component, the exhaust-gas-purifying catalyst of the present invention is good in terms of the durability, and has a high NO_x purifying capability after a durability test.

[0048] The alkali component referred herein means an alkali metal and an alkaline-earth metal, as for the alkali metal, lithium, sodium, potassium, rubidium, cesium and francium are listed. Further, the alkaline-earth metal means the group 2A elements in the periodic table of the elements, barium, beryllium, magnesium, calcium and strontium are listed.

[0049] The alkali component can preferably be loaded in an amount of 0.01-2 mol with respect to 100 parts by weight of the first zeolite. When the loading amount of the alkali component is less than 0.01 mol, it is difficult to suppress the SO_x poisoning of the catalyst metal, when it is loaded in an amount of more than 2 mol, there might arise a case where the NO_x purifying capability decreases.

[0050] In the exhaust-gas-purifying catalyst set forth in Claim 5, the second zeolite can preferably be mixed in an amount of 30-500 parts by weight with respect to 100 parts by weight of the first zeolite. When the mixed amount of the second zeolite is less than 30 parts by weight, the HC adsorbing capability and the cracking capability are decreased so that the NO_x purifying capability decreases, when it is more than 500 parts by weight, the content of the first zeolite decreases relatively to decrease the contents of the catalyst metal and the alkali component so that the NO_x purifying capability decreases.

[0051] Note that it is preferred that nothing is loaded on the second zeolite, however, depending on cases, a part or all of the catalyst metal can be loaded. With this arrangement, the SO_x poisoning of the noble metal is likely to occur, but since the reactivity between the released HC and the NO_x is improved, the initial NO_x purifying capability is improved.

[0052] When producing the exhaust-gas-purifying catalyst set forth in Claim 5, the catalyst metal and the alkali component are first loaded on the first zeolite by an ordinary method, thereby making a loaded first zeolite. The second zeolite free from loading is mixed with this loaded first zeolite to make a mixture powder, the mixture powder is made into a slurry, and a honeycomb catalyst can be produced by coating and burning the slurry on a honeycomb support substrate.

[0053] According to the exhaust-gas-purifying catalyst set forth in Claim 6, in the exhaust-gas-purifying catalyst set forth in Claim 1, the first zeolite which has a large molar ratio (Si/Al) is used. In the first zeolite which has a large molar ratio (Si/Al), since there are less acidic sites, the HC adsorbing capability is low. However, since the de-Al hardly occurs, the granular growth of the catalyst metal resulting from the de-Al is suppressed, and the durability is improved. Further, by the de-Al, the chronological decrement of the HC adsorbing ability is inhibited.

[0054] Whilst, the second zeolite has a smaller molar ratio (Si/Al) than the first zeolite. Since the zeolite, which has

such a smaller molar ratio (Si/Al), has a large number of acidic sites, it is good in terms of the HC adsorbing capability.

[0055] And, the catalyst metal is loaded on the first zeolite. Accordingly, since the de-Al hardly occurs, the granular growth of the catalyst metal is suppressed during the service, and since the initial activity is maintained for a long period of time, the present exhaust-gas-purifying catalyst is good in terms of the durability of the NO_x purifying capability.

5 [0056] In the exhaust-gas-purifying catalyst set forth in Claim 6, when the difference is a bit between the molar ratios (Si/Al) of the first zeolite and the second zeolite, the effect is obtained to a certain extent, but it is preferred that 200 or more is given to the difference.

[0057] In the exhaust-gas-purifying catalyst set forth in Claim 6, it is preferred that the ratio of the first zeolite with respect to the second zeolite falls in the range of the first zeolite/the second zeolite = 2/3-1/2 by weight. When the first
10 zeolite is smaller than this range, since the catalyst metal is loaded on the first zeolite with a high density, the granular growth is likely to occur unpreferably. Further, when the second zeolite is smaller than this range, the HC adsorbing capability decreases so that NO_x purifying capability decreases unpreferably.

[0058] As for the first zeolite and the second zeolite, it is possible to use an independent species selected from a plurality of zeolites, and a plurality of them can be mixed to use. In the latter case, they are selected and used so that
15 the average value of the molar ratio (Si/Al) is larger in the first zeolite than in the second zeolite.

[0059] However, in view of the structural stability, it is preferable for the first zeolite to use mordenite exhibiting 200 or more, ZSM-5 exhibiting 1,000 or more, type "Y" zeolite exhibiting 400 or more, type "A" zeolite exhibiting 400 or more, ferrierite exhibiting 400 or more, or zeolite β exhibiting 200 or more by a molar ratio (Si/Al). The molar ratio (Si/Al) of the
20 zeolite is smaller than these values, the granular growth of the catalyst metal is likely to occur by the changes of the zeolite structures during the service, and the durability of the NO_x purifying ability decreases.

Preferred Embodiments

[0060] Hereinafter, the present invention will be described in detail with reference to examples and comparative
25 examples. Note that, unless otherwise specified, the word "parts" shall hereinafter mean parts by weight.

(Example No. 1)

[0061] 100 parts of a commercially available ZSM-5 powder (ZSM5-40: "HSZ840HOA" made by Tohso Co., Ltd.,
30 Si/Al ratio = 40, an average pore diameter 5.5 Å) was prepared, was mixed with 100 parts of a hexaammine platinum hydroxide salt aqueous solution having a concentration of 3% by weight and 200 parts of pure water, and was stirred for 1 hour. Thereafter, the mixture was kept to be heated at 100 °C to evaporate and dry, was dried at 120 °C for 2 hours, and was burned at 300 °C for 2 hours, thereby preparing a first zeolite powder loaded with Pt in an amount of 3.0% by weight.

35 [0062] Whilst, an unloaded mordenite powder (Mor30: "HSZ660HOA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.0 Å) was taken as a second zeolite powder.

[0063] Next, 50 parts of the first zeolite powder with Pt loaded, 100 parts of the aforementioned second zeolite, 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry.

40 [0064] Then, a honeycomb support substrate (volume 1.5 L) made from cordierite was prepared, was immersed into the slurry, was thereafter taken up therefrom, and was blown to remove the excessive slurry, was dried at 100 °C for 2 hours, and was thereafter burned at 500 °C for 2 hours, thereby obtaining a catalyst of Example No. 1. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to
45 1 L of the support substrate.

(Example No. 2)

[0065] Except that 100 parts of a mordenite powder (Mor203: "HSZ690HOA" made by Tohso Co., Ltd., Si/Al ratio = 203, an average pore diameter 7.0 Å) was used as the second zeolite powder instead of Mor30, a catalyst of Example
50 No. 2 was prepared in the same manner as Example No. 1. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Example No. 3)

55 [0066] Except that 100 parts of a type "Y" zeolite powder (USY-30: "HSZ370HUA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.8 Å) was used as the second zeolite powder instead of Mor30, a catalyst of Example No. 3 was prepared in the same manner as Example No. 1. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Example No. 4)

- 5 [0067] Except that 100 parts of a type "Y" zeolite powder (USY-400: "HSZ390HUA" made by Tohso Co., Ltd., Si/Al ratio = 400, an average pore diameter 7.8 Å) was used as the second zeolite powder instead of Mor30, a catalyst of Example No. 4 was prepared in the same manner as Example No. 1. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Example No. 5)

- 10 [0068] Except that 100 parts of a ZSM-5 powder (ZSM5-2000: "HSZ890HOA" made by Tohso Co., Ltd., Si/Al ratio = 2000, an average pore diameter 5.5 Å) was used as the first zeolite powder, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 1.
 [0069] And, the first zeolite powder loaded with Pt and the second zeolite powder same as that of Example No. 1 were used, and were coated in the same manner as Example No. 1, thereby preparing a catalyst of Example No. 5. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Example No. 6)

- 20 [0070] Except that 100 parts of a ZSM-5 powder (ZSM5-2000: "HSZ890HOA" made by Tohso Co., Ltd., Si/Al ratio = 2000, an average pore diameter 5.5 Å) was used as the first zeolite powder, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 1.
 [0071] Whilst, an unloaded mordenite powder (Mor203: "HSZ690HOA" made by Tohso Co., Ltd., Si/Al ratio = 203, an average pore diameter 7.0 Å) was made into a second zeolite powder.
 25 [0072] And, they were coated in the same manner as Example No. 1, thereby preparing a catalyst of Example No. 6. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Example No. 7)

- 30 [0073] Except that 100 parts of a mordenite powder (Mor30: "HSZ660HOA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.0 Å) was used as the first zeolite powder, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 1.
 [0074] Whilst, an unloaded type "Y" zeolite powder (USY-30: "HSZ370HUA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.8 Å) was made into a second zeolite powder.
 35 [0075] And, they were coated in the same manner as Example No. 1, thereby preparing a catalyst of Example No. 7. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

40 (Example No. 8)

- [0076] Except that 100 parts of a mordenite powder (Mor203: "HSZ690HOA" made by Tohso Co., Ltd., Si/Al ratio = 203, an average pore diameter 7.0 Å) was used as the first zeolite powder, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 1.
 45 [0077] Whilst, an unloaded type "Y" zeolite powder (USY30: "HSZ370HUA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.8 Å) was made into a second zeolite powder.
 [0078] And, they were coated in the same manner as Example No. 1, thereby preparing a catalyst of Example No. 8. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

50

(Example No. 9)

- [0079] Except that 100 parts of a ferrierite powder (Fer17: "HSZ720HOA" made by Tohso Co., Ltd., Si/Al ratio = 17, an average pore diameter 4.8 Å) was used as the first zeolite powder, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 1.
 55 [0080] Whilst, an unloaded ZSM-5 powder (ZSM5-40: "HSZ840HOA" made by Tohso Co., Ltd., Si/Al ratio = 40, an average pore diameter 5.5 Å) was made into a second zeolite powder.
 [0081] And, they were coated in the same manner as Example No. 1, thereby preparing a catalyst of Example No.

9. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Example No. 10)

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[0082] Except that 100 parts of a ferrierite powder (Fer17: "HSZ720HOA" made by Tohso Co., Ltd., Si/Al ratio = 17, an average pore diameter 4.8 Å) was used as the first zeolite powder, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 1.

10 [0083] Whilst, an unloaded ZSM-5 powder (ZSM5-2000: "HSZ890HOA" made by Tohso Co., Ltd., Si/Al ratio = 2000, an average pore diameter 5.5 Å) was made into a second zeolite powder.

[0084] And, they were coated in the same manner as Example No. 1, thereby preparing a catalyst of Example No. 10. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

15 (Example No. 11)

[0085] Except that 100 parts of a ferrierite powder (Fer17: "HSZ720HOA" made by Tohso Co., Ltd., Si/Al ratio = 17, an average pore diameter 4.8 Å) was used as the first zeolite powder, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 1.

20 [0086] Whilst, an unloaded mordenite powder (Mor30: "HSZ660HOA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.0 Å) was made into a second zeolite powder.

[0087] And, they were coated in the same manner as Example No. 1, thereby preparing a catalyst of Example No. 11. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

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(Example No. 12)

30 [0088] Except that 100 parts of a ferrierite powder (Fer17: "HSZ720HOA" made by Tohso Co., Ltd., Si/Al ratio = 17, an average pore diameter 4.8 Å) was used as the first zeolite powder, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 1.

[0089] Whilst, an unloaded mordenite powder (Mor203: "HSZ690HOA" made by Tohso Co., Ltd., Si/Al ratio = 203, an average pore diameter 7.0 Å) was made into a second zeolite powder.

35 [0090] And, they were coated in the same manner as Example No. 1, thereby preparing a catalyst of Example No. 12. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Example No. 13)

40 [0091] Except that 100 parts of a ferrierite powder (Fer17: "HSZ720HOA" made by Tohso Co., Ltd., Si/Al ratio = 17, an average pore diameter 4.8 Å) was used as the first zeolite powder, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 1.

[0092] Whilst, an unloaded type "Y" zeolite powder (USY30: "HSZ370HOA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.8 Å) was made into a second zeolite powder.

45 [0093] And, they were coated in the same manner as Example No. 1, thereby preparing a catalyst of Example No. 13. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Example No. 14)

50 [0094] Except that 100 parts of a ZSM-5 powder (ZSM5-40: "HSZ840HOA" made by Tohso Co., Ltd., Si/Al ratio = 40, an average pore diameter 5.5 Å) was used as the first zeolite powder, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 1.

[0095] Whilst, an unloaded mordenite powder (Mor30: "HSZ660HOA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.0 Å) was made into a second zeolite powder.

55 [0096] Next, 75 parts of the first zeolite powder with Pt loaded, 75 parts of the aforementioned second zeolite, 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry.

[0097] Then, a honeycomb support substrate (volume 1.5 L) made from cordierite was prepared, was immersed

into the slurry, was thereafter taken up therefrom, and was blown to remove the excessive slurry, was dried at 100 °C for 2 hours, and was thereafter burned at 500 °C for 2 hours, thereby obtaining a catalyst of Example No. 14. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

- 5 [0098] Namely, except that the mixing ratio of the first zeolite powder and the second zeolite powder differed, a catalyst of this example had the identical arrangement as that of the catalyst of Example No. 1.

(Example No. 15)

- 10 [0099] Except that 100 parts of a ZSM-5 powder (ZSM5-40: "HSZ840HOA" made by Tohso Co., Ltd., Si/Al ratio = 40, an average pore diameter 5.5 Å) was used as the first zeolite powder, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 1.

[0100] Whilst, an unloaded mordenite powder (Mor30: "HSZ660HOA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.0 Å) was made into a second zeolite powder.

- 15 [0101] Next, 100 parts of the first zeolite powder with Pt loaded, 50 parts of the aforementioned second zeolite, 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry.

[0102] Then, a honeycomb support substrate (volume 1.5 L) made from cordierite was prepared was immersed into the slurry, was thereafter taken up therefrom, and was blown to remove the excessive slurry, was dried at 100 °C for 2 hours, and was thereafter burned at 500 °C for 2 hours, thereby obtaining a catalyst of Example No. 15. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

- 20 [0103] Namely, except that the mixing ratio of the first zeolite powder and the second zeolite powder differed, a catalyst of this example had the identical arrangement as those of the catalysts of Example No. 1 and Example No. 14.

25

(Example No. 16)

[0104] 100 parts of a commercially available type "Y" zeolite powder (USY30: "HSZ370HUA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.8 Å) was prepared, was mixed with 100 parts of a hexaammine platinum hydroxide salt aqueous solution having a concentration of 3% by weight and 200 parts of pure water, and was stirred for 1 hour. Thereafter, the mixture was kept to be heated at 100 °C to evaporate and dry, was dried at 120 °C for 2 hours, and was burned at 300 °C for 2 hours, thereby preparing a zeolite powder loaded with Pt in an amount of 3.0% by weight.

[0105] Next, 50 parts of the zeolite powder with Pt loaded, 100 parts of an unloaded ZSM-5 powder (ZSM5-40: "HSZ840HOA" made by Tohso Co., Ltd., Si/Al ratio = 40, an average pore diameter 5.5 Å), 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry.

[0106] Then, a honeycomb support substrate (volume 1.5 L) made from cordierite was prepared, was immersed into the slurry, was thereafter taken up therefrom, and was blown to remove the excessive slurry, was dried at 100 °C for 2 hours, and was thereafter burned at 500 °C for 2 hours, thereby obtaining a catalyst of Example No. 16. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

40

(Comparative Example No. 1)

45 [0107] 100 parts of a commercially available γ -alumina powder was prepared, was mixed with 100 parts of a hexaammine platinum hydroxide salt aqueous solution having a concentration of 3% by weight and 200 parts of pure water, and was stirred for 1 hour. Thereafter, the mixture was kept to be heated at 100 °C to evaporate and dry, was dried at 120 °C for 2 hours, and was burned at 300 °C for 2 hours, thereby preparing an alumina powder loaded with Pt in an amount of 3.0% by weight.

50 [0108] Next, 50 parts of the alumina powder with Pt loaded, 100 parts of an unloaded mordenite powder (Mor30: "HSZ660HOA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.0 Å), 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry.

[0109] Then, a honeycomb support substrate (volume 1.5 L) made from cordierite was prepared, was immersed into the slurry, was thereafter taken up therefrom, and was blown to remove the excessive slurry, was dried at 100 °C for 2 hours, and was thereafter burned at 500 °C for 2 hours, thereby obtaining a catalyst of Comparative Example No. 1. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

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(Comparative Example No. 2)

[0110] 100 parts of a commercially available titania powder was prepared, was mixed with 100 parts of a hexaamine platinum hydroxide salt aqueous solution having a concentration of 3% by weight and 200 parts of pure water, and was stirred for 1 hour. Thereafter, the mixture was kept to be heated at 100 °C to evaporate and dry, was dried at 120 °C for 2 hours, and was burned at 300 °C for 2 hours, thereby preparing a titania powder loaded with Pt in an amount of 3.0% by weight.

[0111] Next, 50 parts of the titania powder with Pt loaded, 100 parts of an unloaded mordenite powder (Mor30: "HSZ660HOA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.0 Å), 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry.

[0112] Then, a honeycomb support substrate (volume 1.5 L) made from cordierite was prepared, was immersed into the slurry, was thereafter taken up therefrom, and was blown to remove the excessive slurry, was dried at 100 °C for 2 hours, and was thereafter burned at 500 °C for 2 hours, thereby obtaining a catalyst of Comparative Example No. 2. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Comparative Example No. 3)

[0113] 100 parts of a commercially available ZSM-5 powder (ZSM5-40: "HSZ840HOA" made by Tohso Co., Ltd., Si/Al ratio = 40, an average pore diameter 5.5 Å) was prepared, was mixed with 100 parts of a hexaamine platinum hydroxide salt aqueous solution having a concentration of 3% by weight and 200 parts of pure water, and was stirred for 1 hour. Thereafter, the mixture was kept to be heated at 100 °C to evaporate and dry, was dried at 120 °C for 2 hours, and was burned at 300 °C for 2 hours, thereby preparing a zeolite powder loaded with Pt in an amount of 3.0% by weight.

[0114] Next, 150 parts of the zeolite powder with Pt loaded, 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry.

[0115] Then, a honeycomb support substrate (volume 1.5 L) made from cordierite was prepared, was immersed into the slurry, was thereafter taken up therefrom, and was blown to remove the excessive slurry, was dried at 100 °C for 2 hours, and was thereafter burned at 500 °C for 2 hours, thereby obtaining a catalyst of Comparative Example No. 3. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Comparative Example No. 4)

[0116] 100 parts of a commercially available mordenite powder (Mor30: "HSZ660HOA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.0 Å) was prepared, was mixed with 100 parts of a hexaamine platinum hydroxide salt aqueous solution having a concentration of 3% by weight and 200 parts of pure water, and was stirred for 1 hour. Thereafter, the mixture was kept to be heated at 100 °C to evaporate and dry, was dried at 120 °C for 2 hours, and was burned at 300 °C for 2 hours, thereby preparing a zeolite powder loaded with Pt in an amount of 3.0% by weight.

[0117] Next, 150 parts of the zeolite powder with Pt loaded, 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry.

[0118] Then, a honeycomb support substrate (volume 1.5 L) made from cordierite was prepared, was immersed into the slurry, was thereafter taken up therefrom, and was blown to remove the excessive slurry, was dried at 100 °C for 2 hours, and was thereafter burned at 500 °C for 2 hours, thereby obtaining a catalyst of Comparative Example No. 4. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Comparative Example No. 5)

[0119] 100 parts of a commercially available type "Y" zeolite powder (USY30: "HSZ370HUA" made by Tohso Co., Ltd., Si/Al ratio = 30, an average pore diameter 7.8 Å) was prepared, was mixed with 100 parts of a hexaamine platinum hydroxide salt aqueous solution having a concentration of 3% by weight and 200 parts of pure water, and was stirred for 1 hour. Thereafter, the mixture was kept to be heated at 100 °C to evaporate and dry, was dried at 120 °C for 2 hours, and was burned at 300 °C for 2 hours, thereby preparing a zeolite powder loaded with Pt in an amount of 3.0% by weight.

[0120] Next, 150 parts of the zeolite powder with Pt loaded, 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry.

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[0121] Then, a honeycomb support substrate (volume 1.5 L) made from cordierite was prepared, was immersed into the slurry, was thereafter taken up therefrom, and was blown to remove the excessive slurry, was dried at 100 °C for 2 hours, and was thereafter burned at 500 °C for 2 hours, thereby obtaining a catalyst of Comparative Example No. 5. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Evaluation Test)

[0122] Each of the aforementioned catalysts was mounted in an exhaust system of a 2,400 c.c. in-line 4-cylinder diesel engine, the number of revolutions was kept constant at 3,600 rpm, the gas temperature was adjusted so that the gas temperature was 600 °C at the inlets of the catalysts by a load, and a durability test was carried out for 25 hours.

[0123] After the durability test, each of the catalysts was mounted in an exhaust system of the same engine as that of the durability test, respectively, as illustrated in Fig. 1, the number of revolutions was varied in the range of 750 rpm-1,500 rpm by varying the load, and the maximum HC and NO_x conversions were measured, respectively, while adding a light oil into the exhaust gas in the range of 800-1,200 ppmC. The results are set forth in Table 1.

TABLE 1

	Zeolite Support				Max Conversion (%)	
	1st Zeolite		2nd Zeolite		NO _x	HC
	Product Name	Pore Dia. (Å)	Product Name	Pore Dia. (Å)		
E. #1	ZSM5-40	5.5	Mor30	7.0	40	86
E. #2	ZSM5-40	5.5	Mor203	7.0	38	85
E. #3	ZSM5-40	5.5	USY30	7.8	36	86
E. #4	ZSM5-40	5.5	USY400	7.8	35	84
E. #5	ZSM5-2000	5.5	Mor30	7.0	36	83
E. #6	ZSM5-2000	5.5	Mor203	7.0	37	84
E. #7	Mor30	7.0	USY30	7.8	35	81
E. #8	Mor203	7.0	USY30	7.8	36	80
E. #9	Fer17	4.8	ZSM5-40	5.5	40	87
E. #10	Fer17	4.8	ZSM5-2000	5.5	38	86
E. #11	Fer17	4.8	Mor30	7.0	41	88
E. #12	Fer17	4.8	Mor203	7.0	37	86
E. #13	Fer17	4.8	USY30	7.8	36	87
E. #14	ZSM5-40	5.5	Mor30	7.0	33	82
E. #15	ZSM5-40	5.5	Mor30	7.0	28	76
E. #16	USY30	7.8	ZSM5-40	5.5	23	72
C.E.#1	Alumina	-	Mor30	7.0	22	71
C.E.#2	Titania	-	Mor30	7.0	21	73
C.E.#3	ZSM5-40	5.5	-	-	24	74
C.E.#4	Mor30	7.0	-	-	25	75
C.E.#5	USY30	7.8	-	-	22	70

[0124] It is understood from Table 1 that the catalyst of Example No. 16 was better than Comparative Example No. 5 in terms of both of the HC conversion and the NO_x conversion, and it is apparent that this is an effect that the arrangement set forth in Claim 1 is employed.

[0125] Further, the catalysts of the other examples exhibited remarkably better results than the comparative exam-

ples in terms of both of the HC conversion and the NO_x conversion. Furthermore, Example No. 3 and Example No. 16 inversely employed the first zeolite and the second zeolite, however, the catalyst of Example No. 3 exhibited markedly high conversions. It is apparent that these results are effected by the arrangement that the average pore diameter of the first zeolite loaded with Pt was smaller than the average pore diameter of the second zeolite.

5 [0126] Moreover, when Example No. 1, Example No. 14 and Example No. 15 were compared, it is understood that the catalyst of Example No. 1 exhibited the highest purifying activity, and that the activities decreased in this order. Namely, it is preferred that the mixing ratio of the first zeolite loaded with Pt and the unloaded second zeolite is small, and, in the range of this example, it is most preferred that the first zeolite/the second zeolite = 1/2.

10 [0127] Namely, in accordance with the exhaust-gas-purifying catalyst set forth in Claim 2, NO_x contained in an oxygen rich exhaust gas can be purified efficiently, and since the HC poisoning of the catalyst metal is suppressed, the durability of the NO_x purifying performance is extremely good, and it is possible to purify NO_x stably for a long period of time.

(Example No. 17)

15 [0128] In Fig. 2, a structure of an exhaust-gas-purifying catalyst according to this example is illustrated schematically. This exhaust-gas-purifying catalyst is constituted by a mixture powder of a ferrierite powder 1, on which Pt 10 and Li 11 are loaded and which works as the first zeolite, and an unloaded mordenite 203 powder 2, which works as the second zeolite. Hereinafter, a production process of this exhaust-gas-purifying catalyst will be described instead of a detailed description of the arrangement.

20 [0129] 120 g of a ferrierite powder was mixed with a predetermined amount of a hexaammine platinum hydroxide aqueous solution having a predetermined concentration, and was stirred for 1 hour. Thereafter, the mixture was kept to be heated at 100 °C to evaporate and dry the water content, was dried at 120 °C for 2 hours, and was burned at 300 °C for 2 hours. Thus, 2 g of Pt was loaded on 120 g of the ferrierite.

25 [0130] Next, the ferrierite powder loaded with Pt was mixed with a predetermined amount of a lithium acetate aqueous solution having a predetermined concentration, and was stirred for 1 hour. Thereafter, the mixture was kept to be heated at 100 °C to evaporate and dry the water content, was dried at 120 °C for 2 hours, and was burned at 300 °C for 2 hours. Thus, Li was loaded in an amount of 0.05 mol with respect to 120 g of the ferrierite, and a zeolite support powder was obtained in which 2 g of Pt and 0.05 mol of Li were loaded on 120 g of the ferrierite.

30 [0131] With respect to a total amount of the thus obtained zeolite support powder, 120 g of a mordenite 203 powder was mixed. And, a slurry was prepared from this mixture powder, a honeycomb support substrate (volume 1.5 L) made from cordierite was prepared, immersed into the slurry, was thereafter taken up therefrom, and was blown to remove the excessive slurry, was dried at 100 °C for 2 hours, and was thereafter burned at 500 °C for 2 hours, thereby forming a coating layer, and a monolithic catalyst of Example No. 1 was obtained. The coating amount was about 122 g with respect to 1 L of the support substrate, the loading amount of Pt was 2 g with respect to 1 L of the support substrate, and the loading amount of Li was about 0.05 mol with respect to 1 L of the support substrate.

(Example No. 18)

40 [0132] Except that a potassium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 18 was prepared in the same manner as Example No. 17. The loading amount of K was about 0.05 mol with respect to 1 L of the support substrate.

(Example No. 19)

45 [0133] Except that a sodium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 19 was prepared in the same manner as Example No. 17. The loading amount of Na was about 0.05 mol with respect to 1 L of the support substrate.

50 (Example No. 20)

[0134] Except that a magnesium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 20 was prepared in the same manner as Example No. 17. The loading amount of Mg was about 0.05 mol with respect to 1 L of the support substrate.

55 (Example No. 21)

[0135] Except that a strontium acetate aqueous solution was used instead of the lithium acetate aqueous solution,

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a monolithic catalyst of Example No. 21 was prepared in the same manner as Example No. 17. The loading amount of Sr was about 0.05 mol with respect to 1 L of the support substrate.

(Example No. 22)

[0136] Except that a barium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 22 was prepared in the same manner as Example No. 17. The loading amount of Ba was about 0.05 mol with respect to 1 L of the support substrate.

(Example No. 23)

[0137] Except that a mixture aqueous solution of potassium acetate and barium acetate was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 23 was prepared in the same manner as Example No. 17. The loading amounts of K and Ba were about 0.025 mol with respect to 1 L of the support substrate, respectively.

(Example No. 24)

[0138] Except that the lithium acetate aqueous solution was not used, and that Li was not loaded, a monolithic catalyst of Example No. 24 was prepared in the same manner as Example No. 17.

(Comparative Example No. 6)

[0139] Except that the lithium acetate aqueous solution was not used, that Li was not loaded, and that the mordenite 203 powder was not mixed, a monolithic catalyst of Comparative Example No. 6 was prepared in the same manner as Example No. 17.

(Example No. 25)

[0140] Except that a mordenite powder was used instead of the ferrierite powder, a monolithic catalyst of Example No. 25 was prepared in the same manner as Example No. 17.

(Example No. 26)

[0141] Except that a mordenite powder was used instead of the ferrierite powder, and that a potassium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 26 was prepared in the same manner as Example No. 17. The loading amount of K was about 0.05 mol with respect to 1 L of the support substrate.

(Example No. 27)

[0142] Except that a mordenite powder was used instead of the ferrierite powder, and that a sodium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 27 was prepared in the same manner as Example No. 17. The loading amount of Na was about 0.05 mol with respect to 1 L of the support substrate.

(Example No. 28)

[0143] Except that a mordenite powder was used instead of the ferrierite powder, and that a magnesium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 28 was prepared in the same manner as Example No. 17. The loading amount of Mg was about 0.05 mol with respect to 1 L of the support substrate.

(Example No. 29)

[0144] Except that a mordenite powder was used instead of the ferrierite powder, and that a strontium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 29 was prepared in the same manner as Example No. 17. The loading amount of Sr was about 0.05 mol with respect to 1 L of

the support substrate.

(Example No. 30)

- 5 [0145] Except that a mordenite powder was used instead of the ferrierite powder, and that a barium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 30 was prepared in the same manner as Example No. 17. The loading amount of Ba was about 0.05 mol with respect to 1 L of the support substrate.

10 (Example No. 31)

- [0146] Except that a mordenite powder was used instead of the ferrierite powder, and that a mixture aqueous solution of potassium acetate and barium acetate was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 31 was prepared in the same manner as Example No. 17. The loading amounts of K and Ba were about 0.025 mol with respect to 1 L of the support substrate, respectively.

(Example No. 32)

- 20 [0147] Except that a mordenite powder was used instead of the ferrierite powder, that the lithium acetate aqueous solution was not used, and that Li was not loaded, a monolithic catalyst of Example No. 32 was prepared in the same manner as Example No. 17.

(Comparative Example No. 7)

- 25 [0148] Except that a mordenite powder was used instead of the ferrierite powder, that the lithium acetate aqueous solution was not used, that Li was not loaded, and that the mordenite 203 powder was not mixed, a monolithic catalyst of Comparative Example No. 7 was prepared in the same manner as Example No. 17.

(Example No. 33)

- 30 [0149] Except that a ZSM-5 powder was used instead of the ferrierite powder, a monolithic catalyst of Example No. 33 was prepared in the same manner as Example No. 17.

(Example No. 34)

- 35 [0150] Except that a ZSM-5 powder was used instead of the ferrierite powder, and that a potassium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 34 was prepared in the same manner as Example No. 17. The loading amount of K was about 0.05 mol with respect to 1 L of the support substrate.

40

(Example No. 35)

- 45 [0151] Except that a ZSM-5 powder was used instead of the ferrierite powder, and that a sodium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 35 was prepared in the same manner as Example No. 17. The loading amount of Na was about 0.05 mol with respect to 1 L of the support substrate.

(Example No. 36)

- 50 [0152] Except that a ZSM-5 powder was used instead of the ferrierite powder, and that a magnesium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 36 was prepared in the same manner as Example No. 17. The loading amount of Mg was about 0.05 mol with respect to 1 L of the support substrate.

55 (Example No. 37)

- [0153] Except that a ZSM-5 powder was used instead of the ferrierite powder, and that a strontium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 37 was prepared.

pared in the same manner as Example No. 17. The loading amount of Sr was about 0.05 mol with respect to 1 L of the support substrate.

(Example No. 38)

[0154] Except that a ZSM-5 powder was used instead of the ferrierite powder, and that a barium acetate aqueous solution was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 38 was prepared in the same manner as Example No. 17. The loading amount of Ba was about 0.05 mol with respect to 1 L of the support substrate.

(Example No. 39)

[0155] Except that a ZSM-5 powder was used instead of the ferrierite powder, and that a mixture aqueous solution of potassium acetate and barium acetate was used instead of the lithium acetate aqueous solution, a monolithic catalyst of Example No. 39 was prepared in the same manner as Example No. 17. The loading amounts of K and Ba were about 0.025 mol with respect to 1 L of the support substrate, respectively.

(Example No. 40)

[0156] Except that a ZSM-5 powder was used instead of the ferrierite powder, that the lithium acetate aqueous solution was not used, and that Li was not loaded, a monolithic catalyst of Example No. 40 was prepared in the same manner as Example No. 17.

(Comparative Example No. 8)

[0157] Except that a ZSM-5 powder was used instead of the ferrierite powder, that the lithium acetate aqueous solution was not used, that Li was not loaded, and that the mordenite 203 powder was not mixed, a monolithic catalyst of Comparative Example No. 8 was prepared in the same manner as Example No. 17.

(Comparative Example No. 9)

[0158] Except that a ZSM-5 powder was used instead of the ferrierite powder, that a potassium acetate aqueous solution was used instead of the lithium acetate aqueous solution, and that the mordenite 203 powder was not mixed, a monolithic catalyst of Comparative Example No. 9 was prepared in the same manner as Example No. 17. The loading amount of K was about 0.05 mol with respect to 1 L of the support substrate.

(Comparative Example No. 10)

[0159] Except that a ZSM-5 powder was used instead of the ferrierite powder, that a strontium acetate aqueous solution was used instead of the lithium acetate aqueous solution, and that the mordenite 203 powder was not mixed, a monolithic catalyst of Comparative Example No. 10 was prepared in the same manner as Example No. 17. The loading amount of Sr was about 0.05 mol with respect to 1 L of the support substrate.

(Evaluation Test)

[0160] The aforementioned respective catalysts were mounted in an evaluation apparatus, an evaluation model gas set forth in Table 2 was flowed under such a condition that a space velocity (SV) was 200,000/hr in order to measure the NO_x conversions, and the respective maximum values were taken as the initial maximum NO_x conversions and are set forth in Table 3 and Fig. 3.

[0161] Further, with respect to the respective catalysts, a durability test was carried out in which a durability model gas set forth in Table 1 was flowed for 3 hours under such conditions that the space velocity (SV) was 200,000/hr and the inlet gas temperature was 650 °C. Thereafter, the NO_x conversions were measured similarly as described above, and the respective maximum values were taken as the maximum NO_x conversions after the durability test and are set forth in Table 3 and Fig. 3.

TABLE 2

5		NO (ppm)	CO (ppm)	CO ₂ (%)	O ₂ (%)	C ₆ H ₁₄ (ppm)	C ₃ H ₆ (ppm)	SO ₂ (ppm)	N ₂
	Evaluation Gas	250	150	6.7	10%	2000	-	-	Balance
10	Durability Gas	250	150	6.7	10%	-	1000	300	Balance

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TABLE 3

First Zeolite	Cat. Metal & Alkali Compo. Loading Amounts										Nordenite203 Loading Amount(g)	Max. NO _x Conversion (%)	
	Pt g	Li mol	K mol	Na mol	Mg mol	Sr mol	Ba mol	Initial	After Durability				
Ferri-erite	E. No. 17	2	0.05	—	—	—	—	—	120	4.3	4.1		
	E. No. 18	2	—	0.05	—	—	—	—	120	4.4	4.2		
	E. No. 19	2	—	—	0.05	—	—	—	120	4.1	4.0		
	E. No. 20	2	—	—	—	0.05	—	—	120	4.0	3.8		
	E. No. 21	2	—	—	—	—	0.05	—	120	3.9	3.7		
Norden-ite	E. No. 22	2	—	—	—	—	—	0.05	120	4.1	4.0		
	E. No. 23	2	—	0.025	—	—	—	0.025	120	4.2	4.1		
	E. No. 24	2	—	—	—	—	—	—	120	4.9	3.3		
	C.E.No.6	2	—	—	—	—	—	—	—	3.9	2.7		
	E. No. 25	2	0.05	—	—	—	—	—	120	4.4	4.3		
	E. No. 26	2	—	0.05	—	—	—	—	120	4.5	4.4		
	E. No. 27	2	—	—	0.05	—	—	—	120	4.5	4.2		
	E. No. 28	2	—	—	—	0.05	—	—	120	4.2	3.9		
	E. No. 29	2	—	—	—	—	0.05	—	120	4.1	3.9		
	E. No. 30	2	—	—	—	—	—	0.05	120	4.3	4.0		
	E. No. 31	2	—	0.025	—	—	—	0.025	120	4.4	4.1		
	E. No. 32	2	—	—	—	—	—	—	120	5.0	3.4		
	C.E.No.7	2	—	—	—	—	—	—	—	4.0	2.7		
	E. No. 33	2	0.05	—	—	—	—	—	120	4.2	4.0		
	E. No. 34	2	—	0.05	—	—	—	—	120	4.3	4.1		
ZSM-5	E. No. 35	2	—	—	0.05	—	—	—	120	4.2	4.0		
	E. No. 36	2	—	—	—	0.05	—	—	120	3.9	3.8		
	E. No. 37	2	—	—	—	—	0.05	—	120	3.7	3.6		
	E. No. 38	2	—	—	—	—	—	0.05	120	4.0	3.8		
	E. No. 39	2	—	0.025	—	—	—	0.025	120	4.1	3.9		
C.E.No.8	E. No. 40	2	—	—	—	—	—	—	120	4.7	3.4		
	C.E.No.8	2	—	—	—	—	—	—	—	3.8	2.9		
	C.E.No.9	2	—	0.05	—	—	—	—	—	3.0	2.9		
C.F.No.10		2	—	—	—	—	0.05	—	—	3.0	2.9		

[0162] According to Table 3 and Fig. 3, the catalyst of Example No. 24 was superior to the catalyst of Comparative Example No. 6 in terms of the NO_x purifying capability, the catalyst of Example No. 32 was superior to the catalyst of Comparative Example No. 7 in terms of the NO_x purifying capability, and the catalyst of Example No. 40 was superior

to the catalyst of Comparative Example No. 8 in terms of the NO_x purifying capability. These results are the effects of the catalyst set forth in Claim 1 in which the first zeolite loaded with the catalyst metal and the second zeolite free from the loading of the catalyst metal are mixed.

5 [0163] Although the catalysts of Comparative Example Nos. 6, 7 and 8, which were free from the loading of the alkali component, exhibited high initial NO_x purifying activities, the NO_x conversions after the durability test decreased to a large extent by the SO_x poisoning. Further, although the catalysts of Comparative Example Nos. 9-10, on which the alkali component was loaded but which do not have the second zeolite, exhibited NO_x conversion decrements, which were resulted from the durability test, less, they exhibited the low initial NO_x conversions.

10 [0164] It is understood that the other catalysts of the respective examples exhibited high initial NO_x conversions, and that they degraded less after the durability test, and this is apparently an effect which results from the loading of the alkali component on the first zeolite and also from mixing the second zeolite.

[0165] Namely, in accordance with the exhaust-gas-purifying catalyst set forth in Claim 5, since NO_x contained in an oxygen rich exhaust gas can be purified efficiently, and since the durability of the NO_x purifying performance is extremely good, it is possible to purify NO_x stably for a long period of time.

15 (Example No. 41)

[0166] 100 parts of a commercially available mordenite powder (Mor 203: "HSZ690HOA" made by Tohso Co., Ltd., Si/Al ratio = 203) was prepared, was mixed with 100 parts of a hexaammine platinum hydroxide salt aqueous solution having a concentration of 3% by weight and 200 parts of pure water, and was stirred for 1 hour. Thereafter, filtering and cleaning were carried out, the mixture was dried at 120 °C for 2 hours, and was burned at 300 °C for 2 hours, thereby preparing a first zeolite powder loaded with Pt in an amount of 3.0% by weight.

[0167] Whilst, an unloaded mordenite powder (Mor30: "HSZ660HOA" made by Tohso Co., Ltd., Si/Al ratio = 30) was made into a second zeolite powder.

25 [0168] Next, 50 parts of the first zeolite powder with Pt loaded, 100 parts of the aforementioned second zeolite, 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry.

[0169] Then, a honeycomb support substrate (volume 1.5 L) made from cordierite was prepared, was immersed into the slurry, was thereafter taken up therefrom, and was blown to remove the excessive slurry, was dried at 100 °C for 2 hours, and was thereafter burned at 500 °C for 2 hours, thereby obtaining a catalyst of Example No. 1. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

35 (Example No. 42)

[0170] Except that, as a second zeolite powder, 100 parts of a mordenite powder (Mor19: "HSZ640HOA" made by Tohso Co., Ltd., Si/Al ratio = 19) was used instead of Mor30, a catalyst of Example No. 42 was prepared in the same manner as Example No. 41. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

40 (Example No. 43)

[0171] Except that, as a first zeolite powder, 100 parts of a ZSM-5 powder (ZSM5-2000: "HSZ890HOA" made by Tohso Co., Ltd., Si/Al ratio = 2000) was used, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 41.

[0172] Whilst, an unloaded ZSM-5 powder (ZSM5-40: "HSZ840HOA" made by Tohso Co., Ltd., Si/Al ratio = 40) was made into a second zeolite powder.

45 [0173] Then, they were coated in the same manner as Example No. 41, thereby preparing a catalyst of Example No. 43. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

50 (Example No. 44)

[0174] Except that, as a first zeolite powder, 100 parts of a ZSM-5 powder (ZSM5-2000: "HSZ890HOA" made by Tohso Co., Ltd., Si/Al ratio = 2000) was used, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 41.

[0175] Whilst, an unloaded ZSM-5 powder (ZSM5-200: "HSZ870HOA" made by Tohso Co., Ltd., Si/Al ratio = 200) was made into a second zeolite powder.

[0176] Then, they were coated in the same manner as Example No. 41, thereby preparing a catalyst of Example No. 44. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

5 (Example No. 45)

[0177] Except that, as a first zeolite powder, 100 parts of a ZSM-5 powder (ZSM5-200: "HSZ870HOA" made by Tohso Co., Ltd., Si/Al ratio = 200) was used, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 41.

10 [0178] Whilst, an unloaded ZSM-5 powder (ZSM5-40: "HSZ840HOA" made by Tohso Co., Ltd., Si/Al ratio = 40) was made into a second zeolite powder.

[0179] Then, they were coated in the same manner as Example No. 41, thereby preparing a catalyst of Example No. 45. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

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(Example No. 46)

[0180] Except that, as a first zeolite powder, 100 parts of a type "Y" zeolite powder (USY400: "HSZ390HUA" made by Tohso Co., Ltd., Si/Al ratio = 400) was used, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 41.

20 [0181] Whilst, an unloaded type "Y" zeolite powder (USY30: "HSZ370HUA" made by Tohso Co., Ltd., Si/Al ratio = 30) was made into a second zeolite powder.

[0182] Then, they were coated in the same manner as Example No. 41, thereby preparing a catalyst of Example No. 46. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

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(Example No. 47)

[0183] Except that, as a first zeolite powder, 100 parts of a type "Y" zeolite powder (USY400: "HSZ390HUA" made by Tohso Co., Ltd., Si/Al ratio = 400) was used, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 41.

30 [0184] Whilst, an unloaded type "Y" zeolite powder (USY15: "HSZ360HUA" made by Tohso Co., Ltd., Si/Al ratio = 15) was made into a second zeolite powder.

[0185] Then, they were coated in the same manner as Example No. 41, thereby preparing a catalyst of Example No. 47. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

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(Example No. 48)

40 [0186] Except that, as a first zeolite powder, 100 parts of a USY30 powder (USY30: "HSZ370HUA" made by Tohso Co., Ltd., Si/Al ratio = 30) was used, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 41.

[0187] Whilst, an unloaded type "Y" zeolite powder (USY400: "HSZ390HUA" made by Tohso Co., Ltd., Si/Al ratio = 400) was made into a second zeolite powder.

45 [0188] 50 parts of this first zeolite powder with Pt loaded, 100 parts of the second zeolite powder, 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry. And, the slurry was coated in the same manner as Example No. 41, thereby preparing a catalyst of Example No. 48. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

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(Example No. 49)

[0189] Except that, as a first zeolite powder, 100 parts of a ZSM-5 powder (ZSM5-40: "HSZ840HOA" made by Tohso Co., Ltd., Si/Al ratio = 40) was used, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 41.

55 [0190] Whilst, an unloaded ZSM-5 powder (ZSM5-2000: "HSZ890HOA" made by Tohso Co., Ltd., Si/Al ratio = 30) was made into a second zeolite powder.

[0191] 50 parts of this first zeolite powder with Pt loaded, 100 parts of the second zeolite powder, 180 parts of pure

water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry. And, the slurry was coated in the same manner as Example No. 41, thereby preparing a catalyst of Example No. 49. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

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(Example No. 50)

[0192] Except that, as a first zeolite powder, 100 parts of a mordenite powder (Mor30: "HSZ660HOA" made by Tohso Co., Ltd., Si/Al ratio = 30) was used, a first zeolite powder loaded with Pt was prepared in the same manner as Example No. 41.

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[0193] Whilst, an unloaded mordenite powder (Mor203: "HSZ690HOA" made by Tohso Co., Ltd., Si/Al ratio = 203) was made into a second zeolite powder.

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[0194] 50 parts of this first zeolite powder with Pt loaded, 100 parts of the second zeolite powder, 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry. And, the slurry was coated in the same manner as Example No. 41, thereby preparing a catalyst of Example No. 50. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

(Comparative Example No. 11)

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[0195] Except that, as a first zeolite powder, 100 parts of a ZSM-5 powder (ZSM5-40: "HSZ840HOA" made by Tohso Co., Ltd., Si/Al ratio = 40) was used, a ZSM-5 powder loaded with Pt was prepared in the same manner as Example No. 41.

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[0196] 150 parts of this ZSM-5 powder with Pt loaded, 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry. And, the slurry was coated in the same manner as Example No. 41, thereby preparing a catalyst of Comparative Example No. 11. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

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(Comparative Example No. 12)

[0197] Except that, as a first zeolite powder, 100 parts of a Mor30 powder (Mor30: "HSZ660HOA" made by Tohso Co., Ltd., Si/Al ratio = 30) was used, a Mor30 powder loaded with Pt was prepared in the same manner as Example No. 41.

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[0198] 150 parts of this Mor30 powder with Pt loaded, 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry. And, the slurry was coated in the same manner as Example No. 41, thereby preparing a catalyst of Comparative Example No. 14. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

40

(Comparative Example No. 13)

[0199] Except that, as a first zeolite powder, 100 parts of a USY30 powder (USY30: "HSZ370HUA" made by Tohso Co., Ltd., Si/Al ratio = 30) was used, a USY30 powder loaded with Pt was prepared in the same manner as Example No. 41.

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[0200] 150 parts of this USY30 powder with Pt loaded, 180 parts of pure water, and 55 parts of a silica sol (solid content 35%) were mixed, and were stirred, thereby preparing a slurry. And, the slurry was coated in the same manner as Example No. 41, thereby preparing a catalyst of Comparative Example No. 13. The coating amount was 150 g with respect to 1 L of the support substrate, and the loading amount of Pt was 1.0 g with respect to 1 L of the support substrate.

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(Evaluation Test)

[0201] Each of the aforementioned catalysts was mounted in an exhaust system of a 2,400 c.c. in-line 4-cylinder diesel engine, the number of revolutions was kept constant at 3,600 rpm, the gas temperature was adjusted so that the gas temperature was 600 °C at the inlets of the catalysts by a load, and a durability test was carried out for 25 hours.

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[0202] After the durability test, each of the catalysts was mounted in an exhaust system of the same engine as that of the durability test, respectively, as illustrated in Fig. 1, the number of revolutions was varied in the range of 750 rpm-

1,500 rpm by varying the load, and the maximum HC and NO_x conversions were measured, respectively, while adding a light oil into the exhaust gas in the range of 800-1,200 ppmC. The results are set forth in Table 4.

TABLE 4

	Zeolite Support		Max. Conversion(%)	
	1st Zeolite	2nd Zeolite	NO _x	HC
E. #41	Mor203	Mor30	40	86
E. #42	Mor203	Mor19	43	88
E. #43	ZSM5-2000	ZSM5-40	38	85
E. #44	ZSM5-2000	ZSM5-200	35	83
E. #45	ZSM5-200	ZSM5-40	36	84
E. #46	USY400	USY30	35	82
E. #47	USY400	USY15	37	84
E. #48	USY30	USY400	19	68
E. #49	ZSM5-40	ZSM5-2000	21	71
E. #50	Mor30	Mor203	22	73
C.E. #11	ZSM5-40	-	24	74
C.E. #12	Mor30	-	25	75
C.E. #13	USY30	-	22	70

[0203] It is understood from Table 4 that the catalysts of Example Nos. 48-50 were inferior to the catalysts of Example No. 46, Example 44 and Example No. 41, respectively, in terms of the NO_x and HC purifying capability, and that they were even inferior to the catalysts of Comparative Example Nos. 11-13. This is believed to result from the arrangement that the molar ratios (Si/Al) of the first zeolites were so small that there occurred the granular growth of Pt by the changes in the zeolite structures during the durability test.

[0204] However, the catalysts of the other examples exhibited better results than the comparative examples in terms of both of the HC conversion and the NO_x conversion. This effect is apparently resulted from the arrangement that the molar ratios (Si/Al) of the first zeolite loaded with Pt were larger than the molar ratios (Si/Al) of the second zeolite.

[0205] Namely, in accordance with the exhaust-gas-purifying catalyst set forth in Claim 6, since NO_x contained in an oxygen rich exhaust gas can be purified efficiently, and since the durability of the NO_x purifying performance is extremely good, it is possible to purify NO_x stably for a long period of time.

Claims

1. A catalyst for purifying an exhaust gas, the catalyst reducing and purifying nitrogen oxides in an oxygen rich atmosphere which contains oxygen more than necessary for oxidizing components to be oxidized in the exhaust gas by hydrocarbon (HC) adsorbed on a zeolite support, wherein:

the exhaust-gas-purifying catalyst is characterized in that said zeolite support comprises a first zeolite loaded with a catalyst metal and a second zeolite free from loading a catalyst metal.

2. The exhaust-gas-purifying catalyst set forth in Claim 1 is characterized in that said first zeolite has pores whose diameters are a predetermined value or less and said second zeolite has pores whose diameters exceed the predetermined value.
3. The exhaust-gas-purifying catalyst set forth in Claim 2 is characterized in that said predetermined value is 5.5 Å.
4. The exhaust-gas-purifying catalyst set forth in Claim 1 is characterized in that said first zeolite is 1/4-1/2 by weight ratio in all zeolites.

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5. The exhaust-gas-purifying catalyst set forth in Claim 1 is characterized in that an alkali component selected from the group consisting of alkali metals and alkaline-earth metals is further loaded on said first zeolite.
- 5 6. The exhaust-gas-purifying catalyst set forth in Claim 1 is characterized in that a molar ratio of silicon with respect to aluminum (Si/Al) is larger in said first zeolite than in said second zeolite.
7. The exhaust-gas-purifying catalyst set forth in Claim 6 is characterized in that a difference between the molar ratio (Si/Al) of said first zeolite and the molar ratio (Si/Al) of said zeolite is 200 or more.
- 10 8. The exhaust-gas-purifying catalyst set forth in Claim 6 is characterized in that said first zeolite is 2/3-1/2 by weight ratio in all zeolites.
9. The exhaust-gas-purifying catalyst set forth in Claim 6 is characterized in that said first zeolite employs mordenite exhibiting 200 or more, ZSM-5 exhibiting 1,000 or more, type "Y" zeolite exhibiting 400 or more, type "A" zeolite exhibiting 400 or more, ferrierite exhibiting 400 or more, or zeolite β exhibiting 200 or more by a molar ratio (Si/Al).
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FIG. 1

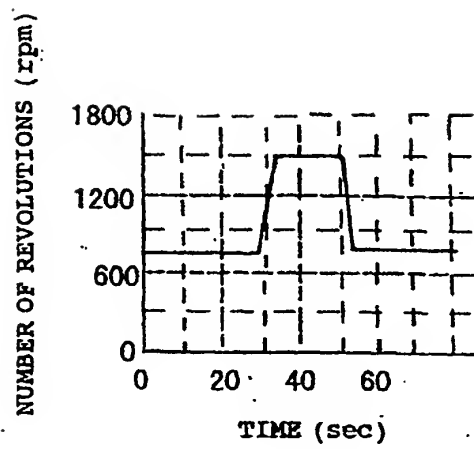
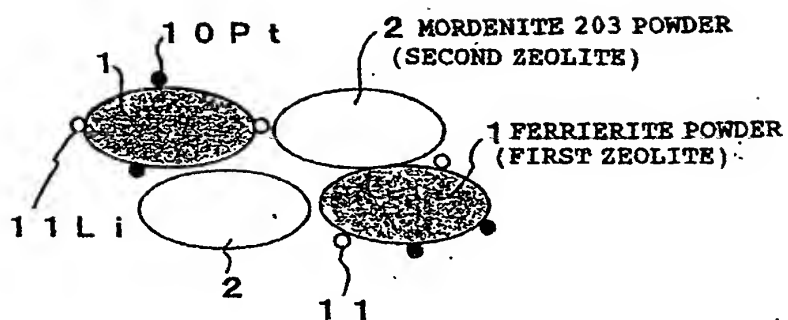
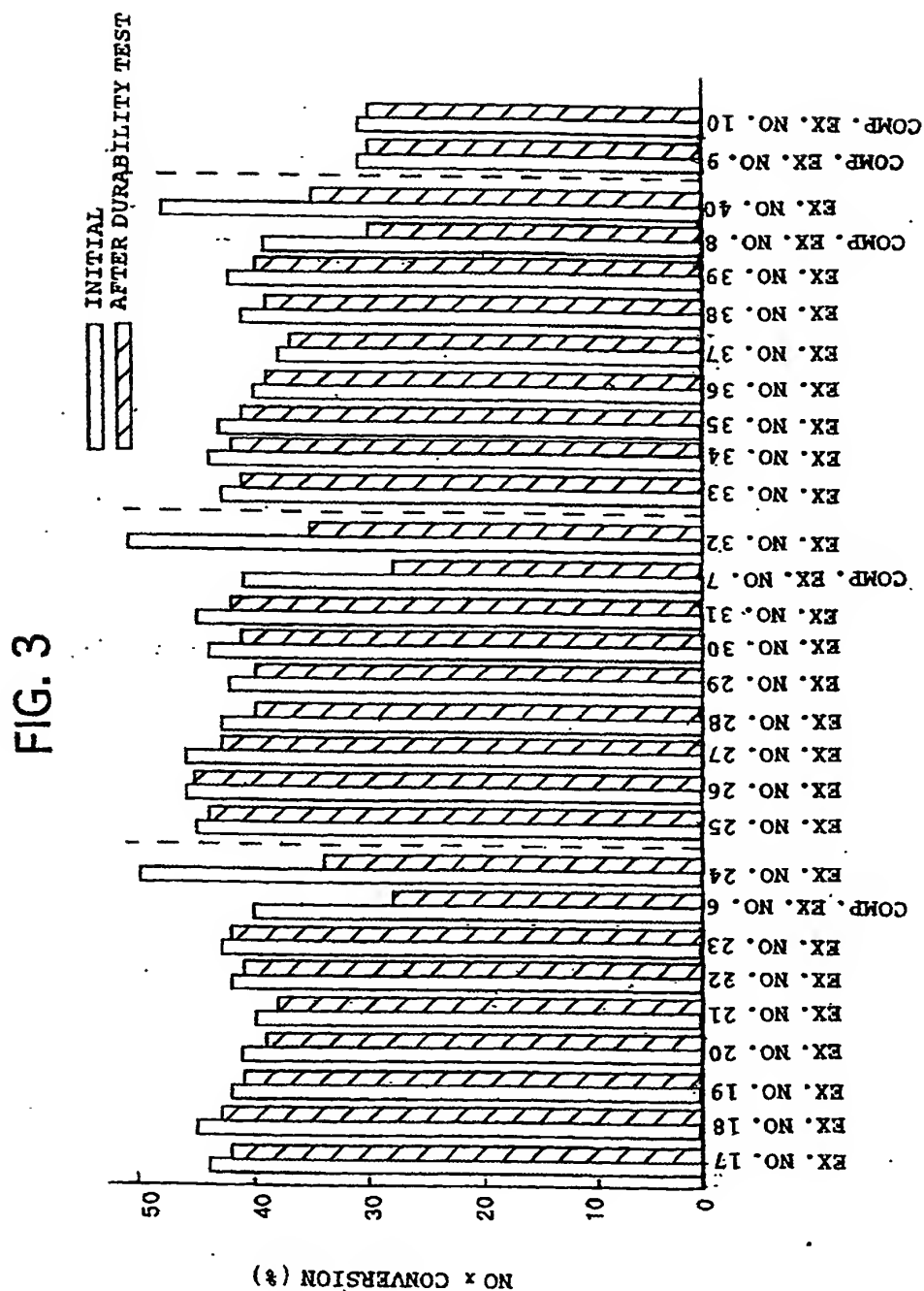


FIG. 2





INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP98/04072

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁶ B01J29/064, B01J29/10, B01J29/20, B01J29/42, B01J29/66, B01D53/94, F01N3/08 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁶ B01J29/064, B01J29/10, B01J29/20, B01J29/42, B01J29/66, B01D53/94, F01N3/08 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1998 Kokai Jitsuyo Shinan Koho 1971-1998 Jitsuyo Shinan Keisai Koho 1996-1998 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 7-155613, A (Nissan Motor Co., Ltd.), 20 June, 1995 (20. 06. 95), Claims ; page 2, column 2, lines 12 to 14 (Family: none)	1-9
X	JP, 5-49933, A (Toyota Motor Corp.), 2 March, 1993 (02. 03. 93), Claims ; page 3, column 3, lines 5 to 13, column 4, lines 1 to 6 (Family: none)	1-3, 5, 6
X	JP, 5-228370, A (Mazda Motor Corp.), 7 September, 1993 (07. 09. 93), Claims ; page 3, column 4, line 30 to page 4, column 5, line 10 ; Examples (Family: none)	1, 4, 5, 8
X	JP, 2-135126, A (Toyota Motor Corp.), 24 May, 1990 (24. 05. 90), Claims ; Examples (Family: none)	1
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the international search 8 December, 1998 (08. 12. 98)		Date of mailing of the international search report 8 December, 1998 (08. 12. 98)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/04072

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 4-267951, A (Kyatara Kogyo K.K.), 24 September, 1992 (24. 09. 92), Claims ; Examples (Family: none)	1, 4, 8
X	JP, 6-327980, A (Petroleum Energy Center), 29 November, 1994 (29. 11. 94), Claims ; page 3, column 4, line 33 to page 4, column 5, line 31 ; Examples (Family: none)	1
X	JP, 2-222727, A (Imperial Chemical Industries PLC), 5 September, 1990 (05. 09. 90), Page 16, lower left column, 7th line from the bottom to lower right column, line 2 ; page 23, lower left column, 8th line from the bottom to lower right column, last line & EP, 378916, A & US, 5041402, A & DE, 68903560, E	1
EX	JP, 10-225635, A (Toyota Motor Corp.), 25 August, 1998 (25. 08. 98), Claims ; page 3, column 4, line 23 to page 4, column 5, line 14 (Family: none)	1, 4, 8
A	JP, 9-215926, A (Institut Francais du Petrole), 19 August, 1997 (19. 08. 97), Claims & FR, 2743733, A & US, 5762902, A	1-9
A	JP, 7-51542, A (Tosoh Corp.), 28 February, 1995 (28. 02. 95), Claims (Family: none)	1-9
A	JP, 5-285392, A (Nissan Motor Co., Ltd.), 2 November, 1993 (02. 11. 93), Claims (Family: none)	1-9

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